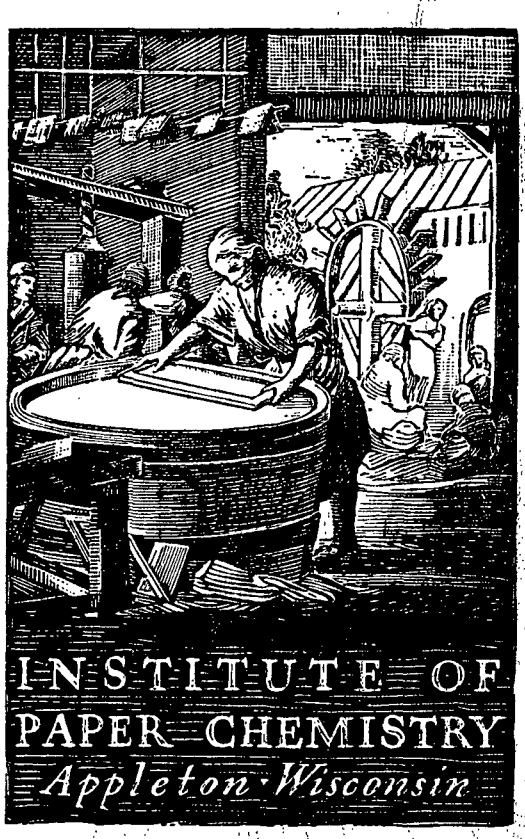

MOLECULAR STRUCTURE OF LIGNOSULFONATES

MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Twelve

A Progress Report

to

PULP MANUFACTURERS RESEARCH LEAGUE

July 29, 1970

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SUMMARY

The prior work on the adhesional and viscomechanical behavior of lignosulfonate adhesive material has shown that these properties are about the same as those of known good plywood adhesives. The work discussed herein shows that the low cohesive strength of the lignosulfonate adhesive, their greatest limitation, can be increased by cross-linking reactions of the phenol-formaldehyde type or of the epoxy type. It was also found that the extent of insolubility in boiling water is a measure of the cross-linking and shows good correlation with plywood bond strength. The boil test can thus serve as a good screening method for potential adhesive use. Finally, it was shown that penetration can deplete the adhesive at the bonding interface and thereby weaken the bond.

Tapered cuts were made at an angle of 1.75° across the glue line of previously tested plywood tensile specimens. The penetration of the lignosulfonate adhesives, as measured by the width of the adhesive color band, is related inversely to the bonding strength, confirming a previous correlation between bond strength and parameters in the Washburn equation of penetration. The viscosity of a plywood adhesive must thus be high (> 20 poise) to minimize penetration into porous wood substrates.

Means of cross-linking lignosulfonates were investigated using selected lignosulfonates and cross-linking agents. The former included lignosulfonates from softwoods and hardwoods, low and high molecular weight fractions, spent sulfite liquors, fractions with and without sugars, fractions with and without salts, ELSA, and heat concentrated ELSA. Cross-linking agents included glyoxal, hexamine,

furfural, and epichlorohydrin. A 30% by weight lignosulfonate solution with cross-linking agent was added to a glass fiber mat and subjected to plywood adhesive curing conditions. Adhesive insolubility in boiling water was determined simultaneously for a large number of samples. Ultimately, insolubility was shown to be directly proportional to adhesive bonding strength, for the limited data obtained. Thus, the boil test appears to be a rapid convenient screening method for lignosulfonate adhesive studies.

In the phenol-formaldehyde-type reaction cross-linking was achieved only with deionized or electrodialyzed lignosulfonic acid (pH < 1) and the better results were with the higher molecular weight products. The limited reactivity of the other materials precluded any judgment of the role of sugars, wood type, or phenolic hydroxyl content (measured from UV difference spectra). Both hexamine and glyoxal show significant reactivity but are far less effective than Catalyn, a phenol-formaldehyde resin.

The epoxy-type reaction with epichlorohydrin as cross-linking agent at pH 12 was effective with a higher molecular weight, sugar-free spruce lignosulfonate and even to some extent with spruce spent sulfite liquor. The former gave the best results of all those tested, with the exception of the Catalyn samples.

The ELSA-Catalyn-wood meal formulation used in previous studies, a corresponding formulation at the same viscosity but with the wood meal left out, and adhesive formulations (including wood meal) selected because of the boil test findings were prepared. Plywood layups were made, cured, and tested. The wood meal *per se* adds significantly ($\sim$ 20%) to the bonding strength either by generating porosity thus controlling penetration, by contributing to the viscomechanical behavior thus aiding stress distribution, and/or by directly contributing to cross-linking through surface hydroxyl groups. Glyoxal is less effective than epichlorohydrin

which is much less effective than Catalyn. Even with a variety of lignosulfonates and cross-linking agents, the bonding results agree favorably with the boil test.

Further work is required to verify the insolubility — bonding strength correlation. An examination of lignosulfonic acids (sources and molecular weights) and Catalyn concentrations should be made so that the optimum conditions can be achieved. In addition, the potential benefits of formaldehyde sources, added phenols, and di-epoxides should be explored. In view of the significant use of lignosulfonates as road binders and the potential similarity to adhesive use, a program is proposed based on the hypothesis that the particle dispersing properties of lignosulfonates are of paramount importance.

INTRODUCTION

This is progress report twelve of Project 2421 entitled "Investigation of the Relationships Between Lignin Structure and its Mechanical and Adhesional Behavior." Up to now the focus of the project has been on the adhesional and mechanical behavior of lignosulfonate adhesives, and their relationship to adhesive bonding strength, particularly in plywood operations. It has been found (1-5) that the surface tension and viscomechanical properties of lignosulfonates are similar to good adhesives, such as phenol-formaldehyde. Thus, the lignosulfonates have good adhesive potential.

The limitations of lignosulfonates as adhesives appear to be due mainly to their low cohesive strength and possibly to some extent their overpenetration into the porous lamina of plywood (5). By implementing cross-linking of the lignosulfonate in the curing operation, it is anticipated that the cohesive strength will increase with more stress being supported by primary bonds, and that the adhesive solubility will decrease with the increased molecular weight. Cross-linking could, thus, achieve increased adhesive bond strength and durability. The major emphasis of the work presented in this report was to clarify avenues of lignosulfonate cross-linking in adhesive operations from both the lignin and the linking agent viewpoints. To this end, a reasonably rapid screening test, based on durability in boiling water, was evaluated. In addition to this work, some effort was given (1) to confirming the role of adhesive penetration on adhesive bond strength, and (2) to evaluating the role of wood meal in the formulation on ultimate bond strength.

The experimental program followed was:

(1) measure adhesive penetration in previous plywood layups from a tapered cut across the glue line,

(2) measure cross-linking of the lignosulfonates by viscosity changes and by water solubility, surveying cross-linking agents and lignosulfonate types.

(3) measure the effect of wood meal on plywood bond strength, and

(4) measure the plywood bond strength of formulations based on significant leads.

EXPERIMENTAL

ADHESIVE PENETRATION MEASUREMENTS

The pieces of the tensile specimens from the layups tested and discussed in Progress Report Eleven (5) were reassembled. A given specimen was then clamped vertically on the bed of a vertical milling machine so that the plane of the glue line was at an angle of 1.75° with respect to the direction of cut. Using a one-inch diameter cutter at the highest rotation, the wood lamina was carefully milled away until the glue line was revealed over about two-thirds of the specimen width. The last few cuts were made at a cutting depth of 0.005 in. in order to minimize wood splintering at the glue line.

The penetration of the adhesive into the lamina was determined by placing a centimeter scale on the tapered cut and estimating the width of the region in which adhesive was evident as judged by the color. This estimate was somewhat subjective because of the varying combinations of spring- and summerwood, the former being more easily penetrated. Ten specimens were examined for each adhesive series. Qualitative comparisons (i.e., ranking) of adhesive penetration based on color were made by visual comparison of the specimens between different adhesives.

LIGNOSULFONATE PHENOLIC HYDROXYL CONTENT

The Goldschmid method (6) was used to determine the phenolic hydroxyl content of the lignosulfonates. A buffer solution of pH 12 was prepared by dissolving 12.4 g. of boric acid in 0.1N sodium hydroxide so that the final volume was 2 liters. Additional sodium hydroxide pellets had to be added to bring the pH to 12.0. Buffer solution at pH 6 was prepared by mixing 495 ml. of 0.2N potassium dihydrogen phosphate solution with 113 ml. of 0.1N sodium hydroxide solution and

diluting to 2 liters with distilled water. A solution containing 0.3 g. of lignosulfonate sample per 100 ml. was prepared using the pH 12 buffer. As soon as the sample was completely dissolved, 2.0-ml. portions of the solution were diluted to 50.0 ml. with pH 12 buffer solution (alkaline solution), and 2.0 ml. of 0.1N sulfuric acid and pH 6 buffer solution (neutralized solution). The ultraviolet difference spectrum was determined by measuring the absorbance of the alkaline solution relative to that of the neutralized solution which was placed in the reference cell of the spectrophotometer (Beckman Model DK-2). This difference spectrum was recorded between 220 to 340 nm. (The original spectra are filed in the Spectroscopy laboratory of The Institute of Paper Chemistry.)

The phenolic hydroxyl group content of the lignosulfonate sample was calculated using the difference spectrum absorbance maximum (Δa_{max}, $\ell.g.^{-1}$ $cm.^{-1}$) at about 300 nm. of the sample and an average extinction coefficient difference for Goldschmid's model compounds ($\Delta\varepsilon_{max} = 4100$) as follows:

$$\text{moles of phenolic hydroxyl per gram} = \Delta a_{max}/4100 \qquad (1)$$

or

$$\text{percentage phenolic hydroxyl} = \Delta a_{max}\ (17/41). \qquad (2)$$

BASIC HYDROLYSIS OF LIGNOSULFONATE

The equivalent of 3.0 g. (o.d. basis) of lignosulfonate was added to 1.0N sodium hydroxide such that the total weight was 100 g. The 250-ml. Erlenmeyer flask in which the solution was contained was fitted with a water cooled condenser for a total reflux condition. The contents were heated to boiling by means of a hot plate and refluxed for 8 hr. In one case, nitrogen gas bubbled through the solution during the entire reflux period and the product was stored in a nitrogen atmosphere until after the phenolic hydroxyl content was determined.

CROSS-LINKING REACTIVITY FROM VISCOSITY

A 5.0-ml. aliquot of a 30% by weight solution of the lignosulfonate was added to a 125 x 15 mm. Pyrex test tube. An air-cooled reflux tube (8 mm. x 12 in., Pyrex) was fitted to the test tube with a rubber stopper. A 5 mm. x 16 in. Pyrex tube was inserted into the reflux tube so that the end was just above the liquid, and it was secured. The test tube was immersed in a boiling water bath such that its contents were just below the bath level and was held in a true vertical position.

Every 5 minutes a viscosity determination was made by the following method: slide the 5-mm. tubing (3 mm. I.D.) down to the bottom of the test tube, seal the upper end with a finger, withdraw the tubing and its contents to just above the liquid level, remove the seal, and measure the time required for the liquid to drain from the tubing. Since the sample volume, test tube dimensions, tubing I.D., and sample temperature are essentially the same for these experiments, the efflux time is proportional to the viscosity of the sample.

CROSS-LINKING REACTIVITY FROM WATER SOLUBILITY

The equivalent of 6.0 g. (o.d. basis) of lignosulfonate was added to the mass of distilled water such that the total water added by whatever means (i.e., a sample already in solution, or cross-linking agent already in solution) was 14.0 g., making a 30 wt.% lignosulfonate solution based only on these components. After the lignosulfonate was dissolved, the desired amount of cross-linking agent was added, based on a weight percent of the mass of lignosulfonate present (e.g., 50% glyoxal means 3.0 g. of pure glyoxal per 6.0 g. of lignosulfonate). The pH was recorded after the cross-linking agent had dissolved. In some cases, as indicated in Table III, p. 20, 0.3M sulfuric acid was used to make the test solutions instead

of distilled water. Also, in some cases concentrated hydrochloric or sulfuric acid was added dropwise to reduce the system to the desired pH. The sulfuric acid caused the precipitation of essentially $CaSO_4$ with about a 5% equivalent weight loss of the original lignosulfonate. The initial sample was accordingly adjusted and the precipitate removed by decanting the mother liquor from the settled mass. Those samples which were run on the alkaline side were prepared by adding enough solid sodium hydroxide pellets to bring the final pH to 12, and in addition, for epichlorohydrin, sufficient sodium carbonate was added to neutralize all of the HCl released in the cross-linking reaction (3.5 g. Na_2CO_3 for 3.0 g. of epichlorohydrin).

Glass fiber mats (934 AH, 5.5-cm. diameter glass fiber filter disk, Reeve Angel, Clifton N.J.), previously conditioned and weighed, were saturated with the lignosulfonate preparation, placed on silicon-treated aluminum foil, and cured at 310°F. at 28 p.s.i., as described previously in Progress Report Eleven (5). Curing times of 5 and 30 min. were employed. After conditioning the disks again to 73°F. and 50% R.H., they were weighed and one of them was selected for the boil test. Tabs were cut from this by placing a 1.5-in. wide metal bar symmetrically on the disk and cutting off the overlapping edges by means of a sharp razor blade. The two tabs were weighed and then placed inside a cotton cloth bag (2-1/2 x 3 in., purchased from Launing Bag & Specialty Co., Harvard, Ill.) which was tied shut by means of cotton string. The bags were placed in the boiling water chamber which had been previously brought to temperature, and kept in this boiling, agitated water for three hours. The boiling chamber consisted of a 12 l. round, flat bottom Pyrex flask with a 17-mm. Pyrex tube attached through the wall at about a level equal to 10-11 liter serving as an overflow vent. Hot water and steam are mixed in a Pyrex tee and introduced by Pyrex tubing to the bottom of the flask by inserting

the tubing through the normal opening in the flask. The hot water and steam are circulated continuously through the flask (placed in a laboratory sink for convenience and safety) during the boil period maintaining a 99+°C. temperature, a continuous state of "rolling" agitation, and a continuous supply of fresh boiling water. At the end of the boil period, cold water is run through the flask. The bags are then removed, laid on blotter stock to aid drainage, carefully opened and turned inside out. The state of the sample is noted and all coherent pieces are carefully removed from a bag and placed in a tared aluminum dish. The pieces are then allowed to dry and condition at 73°F. and 50% R.H., and a final weight is taken.

The percentage of adhesive insolubility was calculated as follows: The weight of adhesive in a disk, $\underline{M_A}$, is

$$M_A = W_A - W_D \qquad (3)$$

where $\underline{W_A}$ and $\underline{W_D}$ are the weights of the disk with and without adhesive, respectively. The weight of adhesive in a piece(s) from this disk, $\underline{m_A}$ is

$$m_A = w_A \, (M_A/W_A) \qquad (4)$$

where $\underline{w_A}$ is the weight of the piece(s) with adhesive before the boil test. The percentage of adhesive insolubility

$$I = ([m_A - (w_A - w_A')]/m_A)100 \qquad (5)$$

where $\underline{w_A}'$ is the weight of the piece(s) after the boil test.

ADHESIVE PREPARATION AND TESTING

Lignosulfonate adhesives were prepared following, in general, the formulation described by Holderby, et al. (7) as given in previous reports (5):

200 g. of 30% lignosulfonate solution, 48 g. of 50% phenol-formaldehyde resin, and 30 g. of 200-mesh wood flour. In each formulation the mass ratio of lignosulfonate to water was maintained at 60:140. In the one case where the wood meal was left out, the viscosity was increased to match and surpass the viscosity of the Holderby formulation (20 poise at room temperature) by autoclaving the original ELSA solution to 10 poise giving 0.3 poise when formulated and finally by heating the final formulation for ten minutes on a steam cone (final viscosity was 100 poise at room temperature — the final formulation did not change viscosity when allowed to stand at room temperature for 3 hours, thus heating was necessary).

Plywood layups were prepared from sanded, aged southern pine veneer as previously described (3). The curing conditions were 310°F. at 150 p.s.i. for 5 min. (the cure time previously used with the formulated adhesive was 4 min. but it was desired to compare the current results with the boil test results which have a 5-min. cure). As with previous work, six layups were made with each adhesive and ten tensile specimens were cut and tested from each layup (3). The amount of wood failure was visually estimated.

RESULTS AND DISCUSSION

ADHESIVE PENETRATION AND BONDING STRENGTH

The linear relationship between plywood bonding strength and parameters from the Washburn equation (liquid penetration into a capillary) found in the previous work (5) suggested that increased penetration reduces the amount of adhesive at the bonding interface which reduces the bond strength. In order to evaluate this concept, previously tested tensile specimens were examined for the extent of adhesive penetration by measuring the adhesive color band width in a tapered cut across the glue line. Ten specimens were examined for each adhesive set. The results are listed in Table I along with the pertinent data from previous work (Progress Report Eleven, Table III, p. 12). Penetration variations due to springwood and summerwood and the fading color variations on a given specimen made the penetration measurements somewhat subjective. However, visual comparisons between composites of the specimens lead to the same conclusions.

In all cases, the adhesive fills the cracks and fissures and natural transport vessels of the wood; the more porous springwood is the region of more penetration compared to the summerwood; and the middle lamina has greater penetration than the outer lamina, due probably to the method of layup preparation (the adhesive is applied to the middle lamina). Greatest penetration is found in Sets 5 and 9, and least in Sets 6 and 10. Set 5 is ELSA and Set 6 is the same ELSA autoclaved to increase the viscosity to that of the formulated adhesive, Set 10. Thus, an increase in viscosity reduces penetration. This observation agrees with previous work [Fig. 1 of Progress Report Eleven (5)]. However, the maximum bond strength of the straight ELSA is still significantly less than that of the formulated adhesive, indicating the need to increase the cohesive strength of the former.

TABLE I

ADHESIVE PENETRATION AND BONDING STRENGTH IN PLYWOOD LAYUPS FROM AGED SOUTHERN PINE VENEER[a]

Set No.	Adhesive	Surface Tension, dynes/cm.	Viscosity, cp.	Bonding Strength, lb./in.^{2}	Adhesive Penetration, cm.	
					Range	Average
5	ELSA No. 66-2, Run 38	44.6	40	62 ± 21	0.4-2.4	1.54
6	Autoclaved ELSA	50.7	664	115 ± 20	0.2-1.4	0.61
7	Autoclaved ELSA, 0.1% Triton X-200	36.2	650	81 ± 14	0.2-1.3	0.93
9	Autoclaved ELSA with 50% hexamethylene-tetramine, 4% glycerin, and 0.1% Triton X-200	33.6	500	42 ± 8	1.0-1.8	1.43
10	Formulated adhesive	42.7	650	260 ± 35	0.3-2.0	0.82

[a]The penetration measurements were made on the tensile specimens from previous work (Table III, p. 12 from Progress Report Eleven), the results of which are included here.

Set 7 is the same autoclaved ELSA as Set 6 but with surfactant added and Set 9 is Set 7 with the cross-linking agent, hexamine (hexamethylene tetramine), and glycerin added. Thus, the surfactant increases penetration, possibly through a decrease in the contact angle, and the bond strength is decreased. The hexamine cross-linking agent increases penetration, perhaps through ammonia gas evolution, decreasing the bond strength still more. It is concluded that, on the porous wood surface, adhesive penetration can reduce the amount of adhesive in the bonding region and thereby reduce the bond strength.

CROSS-LINKING LIGNOSULFONATES

In order to increase the cohesive strength of a lignosulfonate adhesive, chemical cross-linking of the system must be implemented. This problem was viewed both from the inherent reactivity of the lignosulfonate and from the reactivity of the cross-linking agents.

The sites of potential cross-linking reactions on lignosulfonates are unsubstituted ring positions ortho to free phenolic hydroxyls, as in phenol-formaldehyde condensations, or direct reaction of free phenolic hydroxyls with ether-forming agents, as in epoxide condensations. In either case, the phenolic hydroxyl is necessary and the primary bond formed is very stable, a necessary criteria for adhesive durability. Thus, the phenolic hydroxyl content of lignosulfonates may be an important criteria to its potential reactivity and may be a property worthy of enhancing.

The phenolic hydroxyl content of a variety of lignosulfonates was determined by the Goldschmid method (6). The results are listed in Table II. These materials were obtained from the Division of Environmental Systems of The Institute of Paper Chemistry and are well documented. They include softwood and

TABLE II

THE PHENOLIC HYDROXYL AND METHOXYL CONTENT OF SELECTED LIGNOSULFONATES (ALL MATERIALS ARE Ca BASE UNLESS SPECIFIED)

Lignosulfonate	Spruce					Birch					Poplar				
	Peak,[a] mμ.	% OH, as is	% OH, base reflux	% OCH_3	Guaiacyl Propane Units, per OH	Peak,[a] mμ.	% OH, as is	% OH, base reflux	% OCH_3	Syringyl Propane Units, per OH	Peak,[a] mμ.	% OH, as is	% OH, base reflux	% OCH_3	Syringyl Propane Units, per OH
Spent sulfite liquor concn.	299	1.01	1.22	--	--	293	1.21	--	--	--	292	1.73	--	--	--
Ultrafiltration reject	299	0.96	1.62	7.4	4.2	293	1.76	--	12.6	2.0	296	1.25[c]	--	13.6	3.0
Ultrafiltration permeate	297	0.54	--	2.9	3.0	--	--	--	--	--	--	--	--	--	--
Methanol insoluble[b]	300	0.99	--	10.1	5.6	296	0.80	--	9.2	3.2	295	1.38	--	9.3	2.4
Methanol soluble[b] (NH_4 salts)	297	1.65	--	6.6	2.2	292	1.79	1.85	12.2	1.9	292	3.00	--	9.8	0.9
Dialysis reject	--	--	--	--	--	--	--	--	--	--	293	1.78	--	12.4	1.9
Toranil B (fermentation residue)	299	0.92	--	7.8	4.7	--	--	--	--	--	--	--	--	--	--
Toranil free acid	298	1.20	--	9.2	4.2	--	--	--	--	--	--	--	--	--	--
Peritan, dialysis reject (Na salt)	299	1.36	--	9.7	3.9	--	--	--	--	--	--	--	--	--	--
65-8-R198 (ELSA)	300	1.16	--	--	--	--	--	--	--	--	--	--	--	--	--
65-24-R45 (ELSA, heat treated)	300	1.28	--	--	--	--	--	--	--	--	--	--	--	--	--
65-24-R44 (ELSA, heat treated)	301	1.10	--	--	--	--	--	--	--	--	--	--	--	--	--
65-24-R44 heat concentrated	299	1.46	--	--	--	--	--	--	--	--	--	--	--	--	--
66-2-R38 (ELSA)	299	1.00	--	--	--	--	--	--	--	--	--	--	--	--	--
64-8-R151 (ELSA)[d]	--	--	--	--	--	--	--	--	--	--	292	1.80	--	--	--
64-8-R151 steam strip[d]	--	--	--	--	--	--	--	--	--	--	293	1.78	--	--	--
Marasperse CB	306	1.29	--	--	--	--	--	--	--	--	--	--	--	--	--

[a] From the ultraviolet difference spectrum.

[b] Sugars are already removed.

[c] NH_4 base.

[d] Mixed spruce and poplar.

hardwood sources, low and high molecular weight fractions, spent sulfite liquors, fractions with and without sugars, fractions with and without salts, ELSA, and heat-treated ELSA. The values both for the difference spectrum peak position, percentage phenolic hydroxyl, and methoxyl content agree in general with those reported by Goldschmid (6) and by Wexler (8). The ratio of guaiacyl propane [or syringyl propane for hardwoods] units per phenolic hydroxyl, as estimated from the methoxyl content (6), is an index of the molecular weight and is consistent with the corresponding fractions supplied, e.g., ultrafiltration reject > ultrafiltration permeate, methanol insoluble > methanol soluble.

The first six materials listed are essentially from the same source for a given wood type. The difference peak for softwoods ranges from 297-300 nm. and for hardwoods from 292-296 nm. with the higher molecular weights having the higher value peak position. These observations are consistent with the Division of Environmental Systems and literature findings (6, 8). The lower molecular weights are higher in phenolic hydroxyls as seen from the methanol soluble and insoluble fraction The same thing is probably true for the ultrafiltration fractions but here the sugars will end up in the low molecular weight fraction (permeate) diluting on a weight basis the effect of increasing phenolic hydroxyls in the aromatic materials. A similar weight factor is probably the cause of the apparent phenolic hydroxyl increase from Torinal B (Ca salt) to its free acid form. There is a possible increase in phenolic hydroxyl content with heat treatment of ELSA as indicated by comparing the heat treated products R198, R45, and R44 with ELSA. It is of interest to note that R38 and R44 have similar phenolic hydroxyl contents, as these are the ELSA's used in the earlier plywood and viscomechanical studies, respectively. The R151 is currently in large supply and was a possibility for extensive studies, however it appears to be more hardwoodlike in its UV spectrum, although it is a mixture.

Steam stripping the SO_2 from the ELSA indicates that SO_2 makes no difference in the measured phenolic hydroxyl content. The UV difference spectrum of Marasperse shows an intense peak at a wavelength greater than 300 nm., which Wexler (8) interprets as due to some phenolic hydroxyl conjugation with a para-carbonyl group, as in vanillin. As Marasperse is a residue from vanillin production this observation is not surprising.

As found by Collins (9), refluxing the softwood lignosulfonate in 1N NaOH for 8 hours shows a significant increase in the phenolic hydroxyl content, particularly with the high molecular weight fraction (ultrafiltration reject). (The sample refluxed and handled under N_2 gave the same results as in air.) Such an increase is not so apparent with the hardwood materials. However, the enhancement of phenolic hydroxyl content is no better than that achieved by the methanol-soluble fraction, so base refluxing appears to be an impractical approach to upgrading lignosulfonate reactivity. Other approaches considered were mild chlorine reaction (10), Fremy Salt reaction (11), and mild peroxyacetic acid oxidation (12). In the former case, the demethoxylation is accompanied by chlorine substitution in the phenol ring which would deactivate phenolic cross-linking reactions. In the latter two cases dihydroxyl benzene products can be made but they are either ortho or para with respect to each other which considerably reduces their formaldehyde-type condensation reactivity. Therefore, lignosulfonate reactivity was evaluated only from the choice of fractions available.

The reactivity of formaldehyde, glyoxal, furfural, hexamine, and toluyl-diisocyanate with a softwood, sodium-base ELSA (65-24-R44) was tested by measuring the viscosity as a function of time at 100°C. of a 30% by weight solution of ELSA with 25% by weight with respect to ELSA of the cross-linking agent. All of these but the last is of the phenol-formaldehyde-type reaction. The [illegible] was from

3 mm. I.D. Pyrex tubing, no significant changes in viscosity were observed in one hour. This observation supports the general consensus in the literature that lignosulfonates are slow to react. A more sensitive viscosity measurement could be made but in view of the desire for an adhesive with a short cure time, orders of magnitude changes of viscosity only have significance.

Since the usual adhesive curing temperature, pressure, and effective concentrations are not possible to achieve in a refluxing-type system, it appears that water solubility of a cured adhesive would be a more significant measure of cross-linking reactivity. The glass fiber mat system, previously used for visco-mechanical measurements (5), provided a convenient method of handling a cured, isolated adhesive. The determination of the water solubility of many samples was expedited by simultaneously boiling as many samples as desired in one large flask through which steam-heated boiling water was passed. Each sample was enclosed in a cotton cloth bag. The solubility (or insolubility) of an adhesive on exposure to boiling water for three hours was calculated from knowledge of the adhesive content of the glass fiber mat specimen and the weights of the samples before and after the boiling water extraction.

Since hexamine had previously been found to impart some insolubility to an ELSA (5), it was chosen as a test cross-linking agent (formaldehyde type) with lignosulfonates selected on the basis of the variety of the data listed in Table II. These were a crude liquor (softwood for maximum guaiacyl content), a high phenolic hydroxyl content (softwood, methanol soluble), a hardwood (poplar, methanol soluble), a sugar free Ca salt (Toranil B), a free acid (Toranil free acid), an ELSE, an ELSA free of SO_2, and a commercial lignosulfonate by product (Marasperse CB). The cure temperature was 310°F. at 28 p.s.i. with pressing times of 5 min. and 30 min. The results are listed in the first group in the composite

Table III. All of them dissolved completely (the glass fibers once freed can pass through the walls of the cloth bag) except the Toranil free acid. This last lignosulfonate in the adhesive mixture was initially a very viscous material which did not soak into the glass fiber mat very much and the boiling water treatment released pieces of intact film free of glass fibers. In this case, the magnitude of the weight changes do not reflect the insolubility although it was visibly evident.

Phenol-formaldehyde condensations to insolubility are generally achieved under acid conditions (13, 14). The above samples were only weakly acidic or neutral so the work was repeated using 0.3M H_2SO_4 as the solvent rather than distilled water. Those lignosulfonate samples which were in the Ca salt form gave insoluble precipitates which probably were mostly calcium sulfate (since Marasperse has no sulfonate groups it is essentially insoluble in acid). However, only the ones without precipitates were repeated. The results are listed in the second group of Table III. In spite of the acid solvent, the hexamine increases pH to only weakly acidic. Therefore the ELSA (R44 which had been heat concentrated) was included for reaction with hexamine and for reaction with glyoxal. All specimens disintegrated except the Toranil free acid and the R44 heat concentrated, where insoluble pieces were left. The loss of material in greater amount than the amount of adhesive present (in effect, giving "negative" insolubility values) indicates that glass fibers are lost with some adhesive loss. So, although the magnitude of insolubility for these samples is not quantitatively realistic, the trends are usable. The longer heating time increases insolubility. The low pH seems to aid insolubilization reactions (compare the two R-44 heat concentrate reactions) and since hexamine has strong buffering capacity, glyoxal was used in subsequent formaldehyde-type reactions.

TABLE III

WATER INSOLUBILITY OF LIGNOSULFONATE SYSTEMS IN GLASS FIBER MATS CURED UNDER PLYWOOD ADHESIVE CONDITIONS
(THE CONCENTRATION OF THE LIGNOSULFONATE IS MAINTAINED IN THE RATIO OF 30 G. TO 70 G. OF WATER)

Lignosulfonate System	pH	Pressing Time, min.	Disk No. 1, g.		Disk No. 2, g.		Disk No. 3, g.		Disk No. 4, g.		Disk No. 5, g.		Boiling Water Insolubility Test			
			Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Disk No.	Before Boil Specimen Weight, g.	After Boil Specimen Weight, g.	Adhesive Insolubility, %
50% Hexamethylene Tetramine Series																
Spruce SSL concn. 70 CI 122 CU	6.82	5.0	0.1660	0.2680	0.1674	0.2756	0.1661	0.2804	0.1638	0.2607	0.1584	0.2727	3 & 4	0.1137	--	--
Spruce, MeOH sol. ammonium salts	7.15	5.0	0.1710	0.2460	0.1681	0.2607	0.1669	0.2620	0.1588	0.2350	0.1672	0.2631	3 & 4	0.1084	--	--
Poplar, MeOH sol. ammonium salts	7.19	5.0	0.1600	0.2312	0.1650	0.2392	0.1603	0.2474	0.1596	0.2535	0.1629	0.2462	3 & 4	0.1094	--	--
Toranil B	6.85	5.0	0.1712	0.2808	0.1820	0.3117	0.1667	0.2946	0.1760	0.2880	0.1673	0.2921	1 & 3	0.1188	--	--
Toranil free acid	5.50	5.0	0.1606	0.3019	0.1618	0.3045	0.1618	0.3077	0.1586	0.3057	0.1587	0.2874	3 & 4	0.1217	Yes	Yes
64-22c-354	5.57	5.0	0.1589	0.2847	0.1614	0.3088	0.1611	0.3180	0.1627	0.2735	0.1612	0.2845	3 & 4	0.1242	--	--
64-22c-354 steam stripped	5.68	5.0	0.1607	0.3013	0.1602	0.2626	0.1587	0.2744	0.1601	0.2963	0.1696	Lost	3 & 4	0.0818 0.0698	--	--
Marasperse CB	8.67	5.0	0.1601	0.2584	0.1582	0.2785	0.1590	0.2721	0.1582	0.2967	0.1615	0.3197	3 & 4	0.0654 0.0733	--	--
Spruce SSL concn. 70 CI 122 CU	6.82	30.0	0.1671	0.2625	0.1673	0.2583	0.1600	0.2580	0.1661	0.2602	0.1666	0.2634	3 & 4	0.0535 0.0531	--	--
Spruce, MeOH sol. ammonium salts	7.15	30.0	0.1696	0.2476	0.1648	0.2488	0.1583	0.2440	0.1685	0.2490	0.1697	0.2511	3 & 4	0.0537 0.0572	--	--
Poplar, MeOH sol. ammonium salts	7.19	30.0	0.1595	0.2305	0.1611	0.2520	0.1661	0.2634	0.1597	0.2437	0.1627	0.2545	3 & 4	0.0596 0.0529	--	--
Toranil B	6.85	30.0	0.1580	0.2544	0.1673	0.2847	0.1593	0.2771	0.1588	0.2572	0.1601	0.2866	3 & 4	0.0586 0.0510	--	--
Toranil free acid	5.50	30.0	0.1610	0.2729	0.1598	0.2868	0.1577	0.2924	0.1568	0.2831	0.1560	0.2872	3 & 4	0.0655 0.0571	--	--
64-22c-354	5.57	30.0	0.1676	0.2736	0.1676	0.2913	0.1690	0.2965	0.1609	0.2806	0.1649	0.2891	3 & 4	0.0674 0.0630	--	--
64-22c-354 steam stripped	5.68	30.0	0.1618	0.2863	0.1601	0.2921	0.1621	0.2690	0.1616	0.2676	0.1621	0.2757	3 & 4	0.0713 0.0707	--	--
Marasperse CB	8.67	30.0	0.1636	0.2723	0.1585	0.2848	0.1618	0.2740	0.1702	0.2674	0.1601	0.2714	3 & 4	0.0599 0.0570	--	--
Lignin dissolved in 0.3 mole H_2SO_4 50% hexmethylene tetramine added																
Toranil free acid	4.8	5.0	0.1598	0.3057	0.1608	0.3312	0.1602	0.3235	0.1591	0.3394	0.1590	0.3565	1	0.0635	--	--
Toranil free acid	4.8	30.0	0.1605	0.3336	0.1610	0.3602	0.1645	0.3605	0.1764	0.3727	0.1790	0.4028	3	0.0733	0.0346	5
Spruce, MeOH sol. ammonium salts	6.0	5.0	0.1614	0.2472	0.1611	0.2678	0.1584	0.2608	0.1607	0.2523	0.1588	0.2702	1	0.0540	--	--

TABLE III (Continued)

WATER INSOLUBILITY OF LIGNOSULFONATE SYSTEMS IN GLASS FIBER MATS CURED UNDER PLYWOOD ADHESIVE CONDITIONS
(THE CONCENTRATION OF THE LIGNOSULFONATE IS MAINTAINED IN THE RATIO OF 30 G. TO 70 G. OF WATER)

Lignosulfonate System	pH	Pressing Time, min.	Disk No. 1, g.		Disk No. 2, g.		Disk No. 3, g.		Disk No. 4, g.		Disk No. 5, g.		Boiling Water Insolubility Test			
			Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Disk No.	Before Boil Specimen Weight, g.	After Boil Specimen Weight, g.	Adhesive Insolubility, %
Spruce, MeOH sol. ammonium salts	5.0	30.0	0.1609	0.2466	0.1603	0.2630	0.1595	0.2661	0.1751	0.2678	0.1597	0.2671	3	0.0575	--	--
Poplar, MeOH sol. ammonium salts	5.0	5.0	0.1582	0.2500	0.1568	0.2605	0.1564	0.2679	0.1564	0.2428	0.1655	0.2777	3	0.0563	--	--
Poplar, MeOH sol. ammonium salts	5.0	30.0	0.1626	0.2604	0.1564	0.2779	0.1570	0.2574	0.1628	0.2481	0.1580	--	3	0.0576	--	--
64-22c-354	5.0	5.0	0.1663	0.2795	0.1591	0.2880	0.1592	0.2905	0.1601	0.2830	0.1591	0.2837	1	0.0601	--	--
64-22c-354	5.0	30.0	0.1637	0.2744	0.1740	0.3142	0.1538	0.2887	0.1571	0.2780	0.1580	0.2968	3	0.0676	--	--
64-22c-354 steam stripped	5.0	5.0	0.1576	0.2981	0.1650	0.2930	0.1574	0.2934	0.1595	0.2587	0.1598	0.2801	3	0.0752	--	--
64-22c-354 steam stripped	5.0	30.0	0.1572	0.2675	0.1749	0.3011	0.1739	0.2957	0.1611	0.2604	0.1596	0.2842	3	0.0652	--	--
R-44 concentrated + 50% Hex in H_2O	5.3	5.0	0.1599	0.2704	0.1598	0.2957	0.1599	0.2718	0.1650	0.2769	0.1606	0.2845	3	0.0635	--	--
R-44 concentrated + 50% Hex in H_2O	5.3	30.0	0.1734	0.2574	0.1623	0.2778	0.1582	0.2719	0.1744	0.2740	0.1754	0.3169	3	0.0680	--	--
R-44 concentrated + 50% glyoxal in H_2O	5.5	5.0	0.1602	Broken	0.1627	0.2594	0.1749	Broken	0.1764	Broken	0.1755	0.2762	5	0.0670	0.0207	Neg.
R-44 concentrated + 50% glyoxal in H_2O	5.5	30.0	0.1620	0.2387	0.1584	0.2427	0.1586	0.2352	0.1605	--	0.1666	0.2555	3	0.0527	0.0369	7
Phenol formaldehyde	--	--	--	--	--	--	--	--	--	--	--	--	--	0.0561[a]	0.0521	78
Formulated adhesive	--	--	--	--	--	--	--	--	--	--	0.1805	0.5315	62	0.0867	0.0805	89
R-44 whole liq. + hexamethylene tetramine	--	--	--	--	--	--	--	--	--	--	0.1648	0.2175	19	0.0498	0.0278	Neg.
50% Glyoxal - (Catalyn REF):																
Toranil free acid + 40% Catalyn (REF)	0.68	5.0	0.1606	0.3403	0.1760	--	0.1740	--	0.1593	0.2959	0.1631	0.3024	5	0.0577	0.0517	77
Toranil free acid	0.58	5.0	0.1594	--	0.1678	--	0.1598	0.2559	0.1568	--	0.1573	0.2591	3	0.0545	0.0282	Neg.
Toranil B	5.55	5.0	0.1743	0.3363	0.1597	0.3200	0.1611	--	0.1737	0.3640	0.1741	--	4	0.0811	--	--

[a] The adhesive content is based on an average adhesive weight to treated disk weight of 0.343 for this specimen.

TABLE III (Continued)

WATER INSOLUBILITY OF LIGNOSULFONATE SYSTEMS IN GLASS FIBER MATS CURED UNDER PLYWOOD ADHESIVE CONDITIONS
(THE CONCENTRATION OF THE LIGNOSULFONATE IS MAINTAINED IN THE RATIO OF 30 G. TO 70 G. OF WATER)

Lignosulfonate System	pH	Pressing Time, min.	Disk No. 1, g.		Disk No. 2, g.		Disk No. 3, g.		Disk No. 4, g.		Disk No. 5, g.		Boiling Water Insolubility Test			
			Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Disk No.	Before Boil Specimen Weight, g.	After Boil Specimen Weight, g.	Adhesive Insolubility, %
Toranil B + 8-drops concn. HCl	0.58	5.0	0.1570	0.2580	0.1582	0.2855	0.1613	0.2774	0.1575	0.2568	0.1590	0.2875	3	0.0502	--	--
Spruce, MeOH sol. ammonium salts + 2-drops concn. HCl	3.06	5.0	0.1582	0.2465	0.1656	0.2721	0.1659	0.2651	0.1585	0.2506	0.1593	0.2774	3	0.0586	--	--
Dialysis reject + 1-drop concn. HCl	3.02	5.0	0.1581	--	0.1773	0.3514	0.1764	0.3100	0.1641	0.3055	0.1584	0.3102	5	0.0732	--	--
Spruce, MeOH insol. + 2-drops concn. HCl	3.00	5.0	0.1635	--	0.1579	--	0.1573	--	0.1585	0.3452	0.1740	--	4	0.0755	--	--
Spruce, Ca base whole liq. concn. + 2-drops concn. HCl	2.70	5.0	0.1635	--	0.1571	0.2927	0.1745	0.3253	0.1607	--	0.1579	0.3194	2	0.0725	--	--
Spruce, Ca base whole liq. concn. precipitate with H_2SO_4	2.50	5.0	0.1605	--	0.1593	0.3192	0.1575	--	0.1574	--	0.1593	0.3335	5	0.0733	--	--
Dialysis reject + 1-drop concn. HCl	3.02	30.0	0.1601	0.2692	0.1739	0.3223	0.1760	0.3142	0.1765	0.2972	0.1613	0.3138	3	0.0633	--	--
Phenol-furfural – epichlorohydrin series:																
Toranil B + 50% glyoxal + concn. H_2SO_4	0.50	5.0	0.1691	0.2858	0.1620	0.3496	0.1698	0.3188	0.1603	0.3175	0.1690	0.3327	3	0.0652	--	--
Deionized MeOH-sol. spruce No. 745-8A + 50% glyoxal	0.70	5.0	0.1623	0.2231	0.1708	0.2586	0.1612	0.2388	0.1613	0.2313	0.1613	0.2508	3	0.0532	--	--
Spruce, MeOH-sol. ammonium salts + 50% glyoxal + 10-drops concn. H_2SO_4	5.1 0.6	5.0	0.1700	0.2436	0.1702	0.2502	0.1624	0.2438	0.1597	0.2400	0.1695	0.2640	3	0.0494	--	--
Deionized MeOH-sol. aspen + 50% glyoxal	0.3	5.0	0.1580	--	0.1668	--	0.1620	--	0.1768	--	0.1639	0.2636	5	0.0584	--	--
ELSA 65-8-198 + 50% glyoxal	1.1	5.0	0.1633	--	0.1591	0.2601	0.1737	0.2671	0.1608	0.2383	0.1739	0.2725	3	0.0582	--	--
ELSA 65-8-198 + 25% glyoxal	1.1	5.0	0.1615	0.2264	0.1624	0.2288	0.1751	0.2525	0.1604	0.2371	0.1648	0.2727	3	0.0555	--	--
ELSA 65-8-198 (freeze dried) + 100% glyoxal	1.1	5.0	0.1750	--	0.1620	--	0.1592	--	0.1735	0.3246	0.1612	--	4	0.0738	--	--
ELSA 65-8-198 + 25% phenol + 50% glyoxal	0.8	5.0	0.1609	--	0.1600	0.2676	0.1600	0.2595	0.1586	0.2508	0.1619	0.2484	5	0.0526	--	--
ELSA 65-8-198 + 50% furfural	0.5	5.0	0.1751	0.2328	0.1621	0.2305	0.1628	--	0.1643	0.2163	0.1632	0.2319	5	0.0520	--	--

TABLE III (Continued)

WATER INSOLUBILITY OF LIGNOSULFONATE SYSTEMS IN GLASS FIBER MATS CURED UNDER PLYWOOD ADHESIVE CONDITIONS
(THE CONCENTRATION OF THE LIGNOSULFONATE IS MAINTAINED IN THE RATIO OF 30 G. TO 70 G. OF WATER)

Lignosulfonate Systems	pH	Pressing Time, min.	Disk No. 1, g.		Disk No. 2, g.		Disk No. 3, g.		Disk No. 4, g.		Disk No. 5, g.		Boiling Water Insolubility Test			
			Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Untrt'd	Trt'd	Disk No.	Before Boil Specimen Weight, g.	After Boil Specimen Weight, g.	Adhesive Insolubility, %
SLSA 64-8-R151 + 50% glyoxal	9.7	5.0	0.1606	--	0.1597	--	0.1588	--	0.1592	--	0.1595	--	No specimen tested			
SLSA deionized ultrafiltration reject, aspen No. 745-8B + 50% glyoxal	9.7	5.0	0.1661	0.3373	0.1709	--	0.1612	--	0.1712	0.2856	0.1618	0.2900	5	0.0663	--	--
Spruce, MeOH insol. + Na_2CO_3 + 50% epichlorohydrin + 3-pellets NaOH	12.2	5.0	0.1628	0.5800	0.1695	0.5602	0.1586	0.5392	0.1592	0.5399	0.1694	0.5682	3	0.1074	0.0676	42
Spruce, Ca base whole liq. concn. + NaOH (4-pellets) + Na_2CO_3 + 50% epichlorohydrin	12.0	5.0	0.1704	--	0.1655	0.4585	0.1572	0.4425	0.1692	0.4532	0.1592	0.4320	5	0.0989	0.0353	Neg.
Spruce, MeOH sol. ammonium salts + 50% glyoxal + 17-pellets NaOH	12.0	5.0	0.1619	0.2946	0.1600	0.3120	0.1593	0.3067	0.1783	0.3330	0.1631	0.3272	4	0.0728	--	--
3.0 g. Epichlorohydrin + 3.5 g. Na_2CO_3 + NaOH	12.0	5.0	0.1607	--	0.1582	--	0.1652	--	0.1586	--	0.1754	--	--	--	--	--

Since there is evidence of glass fiber loss in the cloth bag — water boil test, three samples tested previously (5) by the single-sample-in-a-beaker — water boil test were tested by the current method. The results are listed in the third group in Table III. Only the pieces from the formulated adhesive were left intact and the results compare favorably: 84 and 89%, respectively, for former and current insolubility values. The original pieces from the phenol-formaldehyde resin broke into several more (they remained intact with former method) and the comparison was not quite as favorable: 97 and 78%, respectively, suggesting some fiber loss with the current method. Only fragmentary pieces were left from the R44-hexamine (quite a bit of disintegration was observed in former run but all solids were contained in the beaker and were recoverable) so the comparison is poor: 20%, negative value, respectively, indicating significant fiber loss with the current method. For samples with high insolubility the former "single" method and the current batch method for measuring insolubility can be quantitative. When insolubility is low (e.g., < 50%) the mechanical action to which the bag is subjected and the porous walls of the cloth bag lead to significant loss of glass fibers, making the bag method insolubility values low. The additional mechanical factor makes the bag method for insolubility potentially a very good screening tool for adhesives. This will be discussed later.

In the fourth group of reactions given in Table III, the effect of acid concentration on cross-linking with glyoxal as the agent, and the reactivity of glyoxal compared to that of Catalyn [the phenol-formaldehyde resin used in the formulated adhesive (7)] were examined. Only the Toranil free acid samples survived the boil test with the Catalyn product showing fairly good insolubility (77%) as compared to the glyoxal product ("negative" value). Thus, glyoxal may improve adhesive strength of the lignosulfonate but not nearly as well as Catalyn. In

comparing the results of the Toranil B samples with that of the Toranil free acid, simply lowering the pH of the salt form of lignosulfonate to that of the free acid does not enhance its reactivity. The results from the other samples tend to support this, although their pH was lowered to just less than 3 which may not be acid enough. Neither the use of HCl or H_2SO_4 to acidify, nor increasing the curing time had any effect on reactivity. The free acid form of lignosulfonate appears to be the more reactive form with formaldehyde-type reactants.

The final group of reactions given in Table III were set up to test (1) the reactivity of the free acid form of various lignosulfonates (the deionization was done by the Division of Environmental Systems) with glyoxal, (2) the reactivity of an ELSA with the formaldehyde-type reactants glyoxal and furfural, (3) the effect of glyoxal concentration on reaction with ELSA, (4) the effect of added phenol on the reaction of glyoxal with ELSA, (5) the reactivity of glyoxal with a lignosulfonate under alkaline conditions (pH = 12), (6) the effect of lowering the pH of lignosulfonate to < 1 with H_2SO_4 (which removes some calcium ions, if present) on reaction with glyoxal, (7) the reactivity of a softwood lignosulfonic acid compared to a hardwood with glyoxal, and (8) the epoxide-type reaction of epichlorohydrin at pH = 12 with a sugar-free lignosulfonate and with a spent sulfite liquor (sufficient Na_2CO_3 was present to neutralize the HCl released in the reaction and thus maintain the pH). All but the epoxide samples failed to survive the boil test. This is quite surprising with regard to the free acid samples. The two previous successes with glyoxal, i.e., Toranil free acid and R44 heat concentrated, were quite viscous in solution compared to the other free acids, suggesting that a high molecular weight free acid is desirable for insolubilizing reactions of the formaldehyde type. These results with free acids should be checked further as, for example, even the sample containing phenol and glyoxal disintegrated. The failure

of reaction of lignosulfonate by simply lowering the pH was reconfirmed even when Toranil B (whose acid form reacts) was treated with H_2SO_4 removing some of the calcium ion. Nothing can be said about the reactivity with regard to formaldehyde-type reactants, soft- vs. hardwood, or reactant concentration.

The epoxide reactions show promising reactivity. The spruce methanol insoluble (sugar free) was 48% insoluble which is the best results with the exception of the Catalyn samples. This sample even showed signs of setting up overnight at room temperature, although the added Na_2CO_3 makes the inert solids content rather high. The fact that spruce spent sulfite liquor shows some insolubilization with epichlorohydrin is very encouraging. A control run was made with the same pH, epichlorohydrin concentration, and Na_2CO_3 content but no lignosulfonate. Only a very small amount of insoluble "grains" remained, suggesting negligible self-polymerization of epichlorohydrin under the reaction conditions. However, the viscosity was very much lower than the sample, limiting the amount of material remaining in the glass fiber mat. Thus, the control should have contained an inert viscosity agent, such as a polyethylene oxide.

ADHESIVE FORMULATION AND THE ROLE OF WOOD MEAL

Based on the insolubilization, the most promising results were included for adhesive formulation and plywood bond strength measurements. The Holderby (7) formulation adhesive (200 parts of 30% ELSA, 48 parts of 50% Catalyn, and 30 parts of 200-mesh wood flour) was used as a control for bonding strength comparisons, as in the previous work. An additional factor studied was the role of wood meal in the formulation. The Holderby receipe was followed in general and the effect of (1) leaving the wood meal out but maintaining the viscosity equal to or greater than the control (done by allowing the ELSA-Catalyn system to react sufficiently before

preparing the layups), (2) replacing Catalyn with glyoxal, (3) using Toranil free acid – glyoxal – wood meal, (4) using spruce methanol insoluble – epichlorohydrin – wood meal (pH 12 buffered with sufficient Na_2CO_3), and (5) using spruce spent sulfite liquor – epichlorohydrin – wood meal (pH = 12 with sufficient Na_2CO_3 buffer). The ELSA (66-2-R38) used in the control, wood meal, and glyoxal runs was the same as that used in the previous plywood studies (3-5). The curing conditions (310°F., 250 p.s.i. for 5 min.) were kept the same as in previous work except the time was changed from 4 to 5 min. so that the results are comparable with the insolubilization studies. The results are listed in Table IV.

The control compares favorably with previous results [222 lb./in.^{2} (3) and 260 lb./in.^{2} (5)]. Since the bonding strength drops by over 20% when the wood meal is left out but viscosity maintained, the wood particles contribute *per se* to bond strength (i.e., in addition to a viscosity increase effect previously discussed). This contribution may be by creating finer porosity than the wood reducing penetration, by aiding stress distribution, and/or by direct cross-linking of the surface groups with the other adhesive components. The use of other particulate materials such as inert-rigid fillers, latices, or active aluminas could be used to investigate this bond strength improvement so that maximum benefit can be achieved. The Catalyn system is much better than that with glyoxal; the Toranil free acid system is somewhat better than that with ELSA; and the methanol insolubles – epichlorohydrin system is much better than that with the spent sulfite liquor (the inert solids introduced with Na_2CO_3 appear to be a bonding detriment, particularly in the latter system). The insolubility data are in agreement with these rankings and, in fact, in quantitative correspondence, as shown in Fig. 1. (The datum point in parentheses is for Toranil free acid – Catalyn insolubility and for ELSA – Catalyn bond strength so, in this case, the lignosulfonates are assumed to be equivalent. The other data

TABLE IV

ADHESIVE FORMULATIONS AND PLYWOOD BONDING DATA
FROM AGED SOUTHERN PINE VENEER

Set No.	Adhesive	Viscosity, (Brookfield, 12 r.p.m.) cp.	pH	Bonding Strength, lb./in.^{2} Layup Average	Bonding Strength, lb./in.^{2} Total Average	Wood Failure, % Layup Average	Wood Failure, % Total Average
1	R38-Catalyn (40%) – wood meal	2,000	0.7	246 194 242 252 246 233	235 ± 47	90 80 85 90 80 90	86
2	R38-Catalyn (40%)	10,000	0.9	162 177 198 192 -- 175	182 ± 31	90 75 90 85 -- 75	83
3	R38-Glyoxal (40%) – wood meal	2,500	0.5	75 138 53 27 95 --	77 ± 47	20 20 25 40 -- 20	25
4	Toranil free acid – glyoxal (50%) – wood meal	gel	0.7	113 137 120 89 37 102	99 ± 47	60 70 60 35 50 60	56
5	Spruce methanol solubles – epichlorohydrin (50%) – wood meal – ($NaOH$, Na_2CO_3)	8,500	11.5	72 97 177 119 124 167	126 ± 49	20 10 25 15 85 85	40
6	Spruce spent sulfite liquor – epichlorohydrin (50%) – wood meal – ($NaOH$, Na_2CO_3)	2,600	11.4	59 27 47 73 -- 60	58 ± 23	0 15 5 5 5 10	8

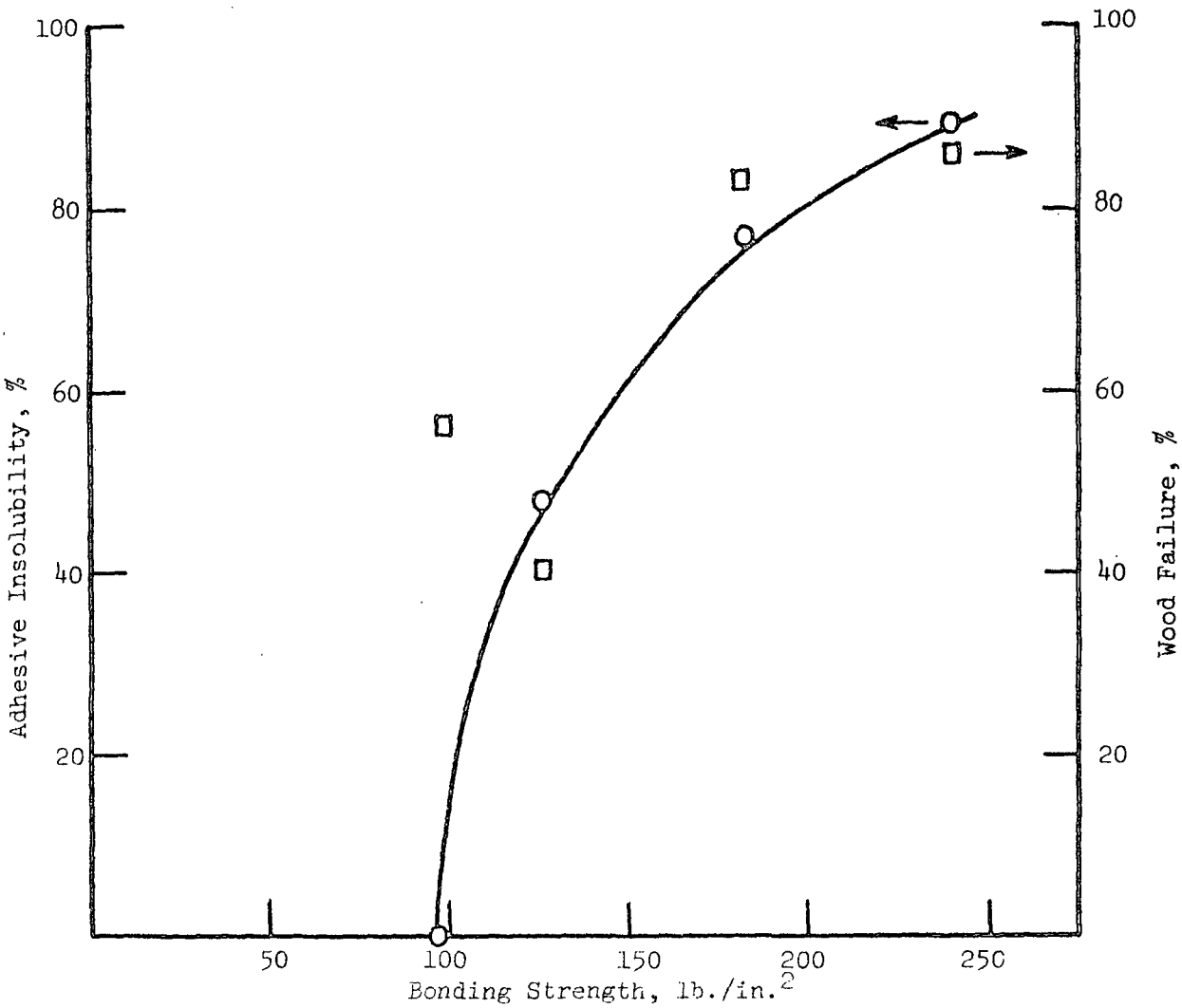

Figure 1. The Relationship Between Adhesive Insolubility, Plywood Bonding Strength, and Wood Failure

are corresponding lignosulfonate — cross-linking agent systems but the wood meal is not present in the insolubility samples.) These few data indicate good correlation between the insolubility data and plywood bond strength data with a variety of systems; thus, insolubility shows promise of being an excellent screening test for potential adhesive use. This point should be confirmed, necessitating additional data. The extent of wood pulled in bond failure (a rather subjective measurement) in general increases with bond strength (see Fig. 1), both achieving a maximum when wood cohesive strength limits the bond strength. Thus, there is a secondary correlation between wood failure and insolubility.

CONCLUSIONS

It is desirable to have only a minimum penetration of adhesive into the porous wood substrate in order to minimize adhesive loss from the bonding region, thus achieving a maximum plywood bond strength. This is done primarily by increasing the viscosity of the adhesive.

The cohesive strength of an adhesive system may be increased by nurturing cross-linking reactions, and boiling water insolubility is a measure of the extent of these reactions. For the few data available, insolubility is directly proportional to plywood bonding strength, and so the solubility measurement could serve as a convenient screening of adhesive potential.

The phenol-formaldehyde-type cross-linking reaction is possible to achieve with plywood adhesive curing conditions when salt-free lignosulfonates are used. As based on a few data, the higher the molecular weights give better results. However, the conditions to cause the single cross-linking agent to give results equivalent to that of a phenol-formaldehyde resin have not yet been achieved.

The epoxy-type cross-linking reaction is possible under plywood adhesive curing conditions, even to some extent with concentrated spent sulfite liquor. This type may have the greater practical use.

The use of wood meal in plywood adhesive formulation has more benefit than only as an agent for increasing viscosity. The causes of added strength should be explained so that maximum benefit is possible.

FUTURE WORK

The development of increased cohesive strength of lignosulfonate adhesives is the most promising avenue for their successful use in plywood particle board, or other bonding systems. The cross-linking reactions should be explored further using the boil test to rapidly screen reactants and conditions (e.g., concentrations, pH, and temperature). In the phenol-formaldehyde-type reactions, the optimum concentration of Catalyn should be sought along with the effect of lignosulfonate type and molecular weight. The condensation polymers of formaldehyde (e.g., trioxane, tetraoxymethylene) should be tried in the phenol-formaldehyde-type reactions, along with the effect of added di- or trifunctional phenols (e.g., resorcinol, phloroglucinol). In the epoxy-type reactions di-epoxide reactants should be used as a way of eliminating the need for Na_2CO_3. If one cannot be found, the best combination of epichlorohydrin concentration and minimum Na_2CO_3 should be sought and the general applicability of this with regard to lignosulfonate source should be examined.

The added strength effect of wood meal should be examined by use of inert fillers, latex fillers, and active aluminas. The viscomechanical properties of the latex may be beneficial to stress distribution if it can be made an integral part of the system.

With the renewed interest in lignosulfonates as road binders, it would seem advisable to extend work into this area, as many properties and criteria of application of lignosulfonates to adhesives may be important here also. Based on information of its use as a road binder, it seems most plausible that it is serving as a very stable dispersant of the soil particles, allowing them to achieve maximum density in the road bed. If this hypothesis is valid, the criteria of their most effective use could be established. Some sorption, viscosity, and

packing density data could speak to this question. Perhaps, while in a state of maximum density, some eventual cross-linking would give the system more cohesive strength, thus allowing it to withstand more abuse.

A specific proposal to these ends has been prepared and submitted.

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APPENDIX I

SURFACE TENSION OF A LOW MOLECULAR WEIGHT LIGNOSULFONATE

It had been previously observed (1) that the lowest molecular weight fraction of an ELSA fractionated by means of gel chromatography had a surface tension (38 dynes/cm. at 73°F. and 34 dynes/cm. at 123°F.) considerably lower than that of the whole material (44 dyne/cm. at 73°F. and 40 dyne/cm. at 123°F.). Thus, a possible means of lowering the surface tension of a lignosulfonate adhesive to make it more compatible with aged southern pine veneer [28 dyne/cm., (3)] is to add an appropriate low molecular weight lignosulfonate.

The lignosulfonates from aspen contain a high percentage of low molecular weights which are methanol extractable. The surface tension of a 10% by weight solution of this fraction was determined by means of a DuNoey Tensiometer and found to be 39 dyne/cm. at 73°F. It was felt that this material did not have a low enough surface tension to warrant further lignosulfonate blending experiments.